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## PATENT ABSTRACTS OF JAPAN

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## (54) LUBRICANT FOR HARD MAGNETIC DISK

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain good lubricating performance, high extreme-pressure performance and good adhesion strength to a diamond-like carbon protective film by using a lubricant essentially comprising a specified phosphagene compd.

SOLUTION: A phosphagene compd. expressed by the formula is used as the main component. In the formula, R is a hydrogen atom, 1-4C alkyl, 1-4C alkoxy or 1-4C haloalkyl group, (a) and (b) are each real numbers 0 to 2, (x) is 1, 2, 3 or 4, (y) is 3 or 4. The phosphagene compd. expressed by the formula is prepared, for example, by the reaction of phosphonitrile halide oligomers and alkali metal salts of phenols or alkali metal salts of fluoroalcohols. As for the phosphonitrile halide oligomers, for example, a phosphonitrile chloride trimer can be used. The obtd. phosphagene compd. as it is may be used as the lubricant.



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JAPANESE

[JP,11-224419,A]

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CLAIMS

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[Claim(s)]

[Claim 1] Lubricant for hard magnetic disks which uses as a principal component the phosphazene compound expressed with a general formula (1).

$[N=P\{O(C_6H_4)R\}_a\{OCH_2(CF_2CF_2)_xH\}_b]_y$  (1)

R is a hydrogen atom, the alkyl of C 1-4, and the halo alkyl of alkoxy \*\*C 1-4 of C 1-4 among [type, a and b are  $a+b=2$  with the real number of 0-2, x is 1, 2, 3, or 4, and y is 3 or 4. ]

[Claim 2] Lubricant according to claim 1 which is the lubricant for hard magnetic disks by which surface coating was carried out by the carbon protective coat.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the lubricant of the hard magnetic disk which is a mass record medium. Furthermore, this invention relates to the surface lubricant of the hard magnetic disk used as a record medium in detail in the recording apparatus of the contact start stop (CSS) method used as the structure where a record medium and the component for record / playback contact at the time of the beginning of using and a halt.

[0002]

[Description of the Prior Art] The Internet, intranet, a Local Area Network, etc. spread and information can be easily taken out only by accessing a network. Although such multimedia age is supported, external storage is in one. The so-called thing of the method with which a record-medium layer is prepared on a circular substrate with high reinforcement (hard disk) as existing mass external storage, high-speed rotation of this hard disk is carried out, and the component for record / playback <a head> operates, and CSS is common, and there are a fixed magnetic disk, an optical disk, a magneto-optic disk, etc. as a hard disk. It is equipment using a fixed magnetic disk which has spread most in these.

[0003]

[Problem(s) to be Solved by the Invention] In order to perform large capacity-ization, without changing the size of these external storage, it is necessary to increase the surface recording density of a record-medium layer. For that, it is required to make bit size small and to bring a head close to a record medium as much as possible. In order to make spacing of a head and a disk small, irregularity on the front face of a disk must be made small, for example, for setting spacing to 100nm or less, irregularity must be set to 10nm or less. And if the smooth nature on the front face of a disk is raised, a head will become easy to stick by one side to a disk side. Moreover, in order to acquire high-speed responsibility, it is necessary to gather the degree of bit \*\*\*\*\*, as a result the rotational speed of a disk. For example, 5400 - 7200rpm is required for the maximum engine speed of a 3.5 inch hard disk, and the head transit rate of a disk periphery has reached 125 km/hr. However, each above modification makes a disk, the contact probability of a head, wear, etc. increase sharply, and makes dependability fall.

[0004] In order to cope with these and to protect a disk front face and a head, the approach of making [ many ] coverage of the lubricant to a disk protective coat front face is the simplest. However, if coverage of lubricant is made [ many ], the sliding friction of lubricating film will increase the absorption of lubricant, and it not only becomes large, but will cause a halt and burning of a spindle motor. If the lubricant of hypoviscosity is used in order to reduce a sliding friction, at the time of high-speed rotation of a disk, lubricant will move and disappear from a protective coat and will cause contact of a disk and a head, and breakage. Lubricant makes the film of lubricant with the uniform thickness of a molecule very simply on the protective coat prepared on the hard disk, and is reducing friction and wear which are produced at the time of hard disk rotation, and starting and a halt of equipment. In order to protect a disk and a head, a sliding friction is small, bonding strength with a protective coat is large, chemical stability, thermal stability, and corrosion resistance are [ it is low coefficient of friction and ] large, it has low-temperature lubrication capacity -10 degrees C or less, and the lubricant in which thin-film[ super-]-izing is possible is required of low vapor pressure. It is that are 20,000 CSS endurance or more and there is no change of coefficient of friction in the lubricant for hard disks. That is, even if it exceeds 20,000 times in a CSS repeat test, there are no abnormalities, such as a blemish, in printing and the disk of a head, and it is required that change of coefficient of friction should be 0.3 or less.

[0005] The diamond-like carbon (DLC, Diamond Like Carbon) protective coat is used for the surface protective coat of the present hard disk from viewpoints, such as chemical stability, reinforcement, thin-film[ super-]-izing, and smooth nature. Since most is carbon so that clearly also from the structure, the protective coat concerned has small chemical affinity, and adhesion force has no choice but to hydrogen base [ which is intermingled slightly ], such as hydrogen bond with a nitrogen atom, and Van der Waals force. Then, as lubricant, perfluoroalkyl polyether oligomer (it abbreviates to "PFPE" below) is common (monthly tribology, the 99 or No. November issue, 37-38 pages, 1995). Although PFPE is equipped with the low surface energy originating in full RUORO carbon, chemical inertness, low vapor pressure, and thermal stability, the bonding strength on low surface energy, therefore the front face of a protective coat is weak, and there is a fault to which lubricant moves and disappears from a protective coat with the centrifugal force of disk rotation. In order to stop this, the additive of the second component is used, but (USP4871625) since [ of low compatibility ] it originates in the fluorocarbon of PFPE, the present condition is that cause phase separation and sufficient effectiveness is not acquired. Then, although there are some

(AUSIMONT K.K., FOMBLIN Z derivative) which introduced functional groups, such as a hydroxyl group and an acyl amide group, into the edge or center section of the PFPE principal chain in order to give affinity to PFPE, the functional group which has these active hydrogen has a possibility of reducing chemical stability by friction with a head. The technical problem of this invention is to offer the lubricant for hard disks which has good CSS endurance.

[0006]

[Means for Solving the Problem] This invention relates to the lubricant for hard magnetic disks which makes an active principle the phosphazene compound expressed with a general formula (1).

$[N=P\{O(C_6H_4)R\}_a\{OCH_2(CF_2CF_2)xH\}_b]_y$  (1)

R is a hydrogen atom, the alkyl of C 1-4, and the halo alkyl of alkoxy \*\*C 1-4 of C 1-4 among [type, a and b are a+b=2 with the real number of 0-2, x is 1, 2, 3, or 4, and y is 3 or 4.]

The good CSS endurance of this invention compound is based on the good adhesion force to the good lubrication engine performance, high extreme pressure engine performance, and DLC protective coat of a compound (1) which have already been shown in many precedence reference, such as Japanese Patent Application No. No. 47680 [ 57 to ]. It is thought that the good adhesion force to a DLC protective coat is based on the synergistic effect of an interaction with a nitrogen atom and the interaction of a phosphazene ring and a DLC protective coat here at the hydrogen list of the hydrogen of a fluorocarbon end and a DLC protective coat by which polarization was carried out with the adjoining fluorine atom.

[0007]

[The mode of implementation of invention] In the phosphazene compound expressed with the general formula (1) of this invention, as alkyl of C 1-4 of R, if C 1-4 carries out alkoxy \*\* of methyl, ethyl, propyl, the butyl, etc., the radical to which a fluorine, chlorine, and a bromine permuted methoxy and ethoxy \*\* propoxy, butoxy one, etc. by the above-mentioned alkyl group as halo alkyl of C 1-4 can be mentioned. These phosphazene compound is a well-known compound given in JP,58-164698,A, JP,62-265394,A, JP,63-103428,A, a U.S. Pat. No. 4613548 specification, etc., for example, can be manufactured by making the oligomer of phospho nitril halide, and the alkali-metal salt of phenols and the alkali-metal salt of fluoro alcohols react. As oligomer of phospho nitril halide, tetramers, etc. such mixture, etc. of the trimer of phospho nitril chloride and phospho nitril chloride can be mentioned here, for example. Moreover, as phenols, a phenol, methyl phenol, a methoxy phenol, a trifluoro methoxy phenol, 3-hydroxy benzo trifluoride, and the other things of a USP [ No. 4613548 ] publication can be mentioned. As fluoro alcohols, the mixture of 1, such as 1, 1, 3-trihydro perfluoro propanol, 1 and 1, and 5-trihydro perfluoro pentanol, 1, omega-trihydro perfluoro alcohol, etc. this, and 2, 2, 3, 3, and 3-pentafluoro propanol etc. can be mentioned, for example. The phosphazene compound of the general formula (1) which has desired a, b, x, and y value is obtained by changing suitably the class and the amount of phenols and the fluoro alcohols used in the case of manufacture.

[0008] In this invention, the phosphazene compound of a general formula (1) can be used as lubricant as it is, or the phosphazene compound of a general formula (1) may be dissolved and used for a suitable organic solvent. As an organic solvent, for example Aromatic hydrocarbon, such as toluene and a xylene, A methylene chloride, chloroform, 1,1,1-trichloroethane, Halogenated hydrocarbon, such as 1,1,2-trichloroethane and trichlorofluoroethane (chlorofluorocarbon 113), The ether, such as diethylether, dimethoxyethane, dioxane, and a tetrahydrofuran, Alicyclic hydrocarbon, such as ester, such as ethyl acetate, ethyl butylate, and amyl acetate, a cyclohexane, cycloheptane, and cyclooctane, dimethylformamide, dimethyl sulfoxide, two or more sorts of these mixed solvents, etc. can be mentioned.

[0009] It is used for the coat by the lubricant of this invention on a DLC protective coat, usually forming. Formation of the coat of this invention lubricant can be carried out with \*\* etc. according to a well-known approach. It faces applying the lubricant of this invention to the hard disk which has a DLC protective coat, and the approach of a spin coat, a DIP coat, etc. is adopted. Although especially the thickness is not restricted, it should just usually make about 10-200Å preferably about 10-50Å. In addition, since adjustment of thickness changes with the vapor pressure of an organic solvent, the concentration of the phosphazene compound of a general formula (1), drying temperature, etc., it can be carried out by choosing the organic solvent to be used suitably or adjusting concentration and drying temperature.

[0010]

[Example] An example and the example of a comparison are given to below, and this invention is explained concretely.

After the hard disk was immersed, it took out, and dried for 30 minutes at 120 degrees C, and the coat of 20-30Å of thickness was formed on the hard disk at the solution which dissolved compound (1)1g given in example 1 table 1 in toluene 500ml. The following trial was presented with this thing. The performance test of lubricant was carried out using the system drive converted so that coefficient of friction could be measured from the force concerning a head by measuring change of coefficient of friction at the time of starting by the CSS repeat test. The head started, where a disk front face is contacted, and the CSS cycle performed the stroke until a head stops again where a disk front face is contacted after the head has surfaced and reaching predetermined engine-speed 3600rpm in 33 seconds, and made this 1 cycle. The texture was made nothing, in order that a hard disk might be what produced the 200-300Å DLC protective coat by plasma CVD and might raise surface smooth nature on the record medium produced by 3.5 inches sputtering. The head set the load to 7.5g by Monolithic MIG (metal in gap). The life judging of a CSS test was taken as the time of a dynamic friction coefficient ( $\mu$ ) exceeding 0.6.

[0011]

[Table 1]

		潤滑剤					低速摩	CSS寿命	ディスクの状態
		化合物(1)					擦係数	(サイクル)	
		a	b	x	y	R	初期	$\mu=0.6$	
実施例	1	1	1	1	3	H	0.183	20000	異常なし
	2	0.5	1.5	2	3	H	0.181	23000	異常なし
	3	1	1	2	3	H	0.184	25000	異常なし
	4	1	1	3	3	H	0.184	28000	異常なし
	5	1	1	4	3	H	0.198	26000	異常なし
	6	1	1	2	4	H	0.195	24000	異常なし
	7	1	1	2	3	CH <sub>3</sub>	0.190	24000	異常なし
	8	1	1	2	3	OCH <sub>3</sub>	0.197	22000	異常なし
	9	1	1	2	3	CF <sub>3</sub>	0.182	29000	異常なし
	10	1	1	3	3	CF <sub>3</sub>	0.185	32000	異常なし
	11	1	1	2	4	CH <sub>3</sub>	0.201	20000	異常なし
比較例	1	0	2	1	3	—	0.133	2600	起動μオーバー
	2	PFPE-OH					0.300	6000	起動μオーバー
	3	NF-10					0.120	2200	起動μオーバー
	4	なし					0.296	10	ヘッド付着、傷

[0012] The permutation location of R is the meta position.

PFPE-OH: F[CF(CF<sub>3</sub>) CF<sub>2</sub>O] nCF(CF<sub>3</sub>) CH<sub>2</sub>OHNF-10:[N=P(OCH<sub>2</sub></SUB>CF<sub>3</sub>)] (OCH<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>) 3 of average molecular weight 2000 [ about ] [0013]

[Effect of the Invention] According to this invention, the lubricant for hard magnetic disks which has good CSS endurance can be offered.

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to the lubricant of the hard magnetic disk which is a mass record medium. Furthermore, this invention relates to the surface lubricant of the hard magnetic disk used as a record medium in detail in the recording apparatus of the contact start stop (CCS) method used as the structure where a record medium and the component for record / playback contact at the time of the beginning of using and a halt.

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**PRIOR ART**

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**EFFECT OF THE INVENTION**

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**TECHNICAL PROBLEM**


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[Problem(s) to be Solved by the Invention] In order to perform large capacity-ization, without changing the size of these external storage, it is necessary to increase the surface recording density of a record-medium layer. For that, it is required to make bit size small and to bring a head close to a record medium as much as possible. In order to make spacing of a head and a disk small, irregularity on the front face of a disk must be made small, for example, for setting spacing to 100nm or less, irregularity must be set to 10nm or less. And if the smooth nature on the front face of a disk is raised, a head will become easy to stick by one side to a disk side. Moreover, in order to acquire high-speed responsibility, it is necessary to gather the degree of bit \*\*\*\*\*, as a result the rotational speed of a disk. For example, 5400 - 7200rpm is required for the maximum engine speed of a 3.5 inch hard disk, and the head transit rate of a disk periphery has reached 125 km/hr. However, each above modification makes a disk, the contact probability of a head, wear, etc. increase substantially, and makes dependability fall.

[0004] In order to cope with these and to protect a disk front face and a head, the approach of making [ many ] coverage of the lubricant to a disk protective coat front face is the simplest. However, if coverage of lubricant is made [ many ], the sliding friction of lubricating film will increase the absorption of lubricant, and it not only becomes large, but will cause a halt and burning of a spindle motor. If the lubricant of hypoviscosity is used in order to reduce a sliding friction, at the time of a high-speed revolution of a disk, lubricant will move and disappear from a protective coat and will cause contact of a disk and a head, and breakage. Lubricant makes the film of lubricant with the uniform thickness of a molecule very simply on the protective coat prepared on the hard disk, and is reducing friction and wear which are produced at the time of a hard disk revolution, and starting and a halt of equipment. In order to protect a disk and a head, a sliding friction is small, bonding strength with a protective coat is large, chemical stability, thermal stability, and corrosion resistance are [ it is low coefficient of friction and ] large, it has low-temperature lubrication capacity -10 degrees C or less, and the lubricant in which thin-film[ super-]-izing is possible is required of low vapor pressure. It is that are 20,000 CSS endurance or more and there is no change of coefficient of friction in the lubricant for hard disks. That is, even if it exceeds 20,000 times in a CSS repeat test, there are no abnormalities, such as a blemish, in printing and the disk of a head, and it is required that change of coefficient of friction should be 0.3 or less.

[0005] The diamond-like carbon (DLC, Diamond Like Carbon) protective coat is used for the surface protective coat of the present hard disk from viewpoints, such as chemical stability, reinforcement, thin-film[ super-]-izing, and smooth nature. Since most is carbon so that clearly also from the structure, the protective coat concerned has small chemical affinity, and adhesion force has no choice but to hydrogen base [ which is intermingled slightly ], such as hydrogen bond with a nitrogen atom, and Van der Waals force. Then, as lubricant, perfluoroalkyl polyether oligomer (it abbreviates to "PFPE" below) is common (monthly tribology, the 99 or No. November issue, 37-38 pages, 1995). Although PFPE is equipped with the low surface energy originating in full RUORO carbon, chemical inertness, low vapor pressure, and thermal stability, the bonding strength on low surface energy, therefore the front face of a protective coat is weak, and there is a fault to which lubricant moves and disappears from a protective coat with the centrifugal force of a disk revolution. Although the additive of the second component is used in order to stop this (USP4871625), the actual condition is that cause phase separation and sufficient effectiveness is not acquired for the low compatibility originating in the fluorocarbon of PFPE. Then, although there are some (AUSIMONT K.K., FOMBLIN Z derivative) which introduced functional groups, such as a hydroxyl group and an acyl amide group, into the edge or center section of the PFPE principal chain in order to give affinity to PFPE, the functional group which has these active hydrogen has a possibility of reducing chemical stability by friction with a head. The technical problem of this invention is to offer the lubricant for hard disks which has good CSS endurance.

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MEANS

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[Means for Solving the Problem] This invention relates to the lubricant for hard magnetic disks which makes an active principle the phosphazene compound expressed with a general formula (1).

$[N=P\{O(C_6H_4)R\}_a\{OCH_2(CF_2CF_2)_xH\}_b]_y$  (1)

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The good CSS endurance of this invention compound is based on the good adhesion force to the good lubricative ability, high extreme pressure engine performance, and DLC protective coat of a compound (1) which have already been shown in many precedence reference, such as Japanese Patent Application No. No. 47680 [ 57 to ]. It is thought that the good adhesion force to a DLC protective coat is based on the synergistic effect of an interaction with a nitrogen atom and the interaction of a phosphazene ring and a DLC protective coat here at the hydrogen list of the hydrogen of a fluorocarbon end and a DLC protective coat by which polarization was carried out with the adjoining fluorine atom.

[0007]

[The mode of implementation of invention] In the phosphazene compound expressed with the general formula (1) of this invention, as alkyl of C 1-4 of R, if C 1-4 carries out alkoxy \*\* of methyl, ethyl, propyl, the butyl, etc., the radical to which a fluorine, chlorine, and a bromine permuted methoxy and ethoxy \*\* propoxy, butoxy one, etc. by the above-mentioned alkyl group as halo alkyl of C 1-4 can be mentioned. These phosphazene compound is a well-known compound given in JP,58-164698,A, JP,62-265394,A, JP,63-103428,A, a U.S. Pat. No. 4613548 description, etc., for example, can be manufactured by making the oligomer of phospho nitril halide, and the alkali-metal salt of phenols and the alkali-metal salt of fluoro alcohols react. As oligomer of phospho nitril halide, tetramers, etc. such mixture, etc. of the trimer of phospho nitril chloride and phospho nitril chloride can be mentioned here, for example. Moreover, as phenols, a phenol, methyl phenol, a methoxy phenol, a trifluoro methoxy phenol, 3-hydroxy benzo trifluoride, and the other things of a USP [ No. 4613548 ] publication can be mentioned. As fluoro alcohols, the mixture of 1, such as 1, 1, 3-trihydro perfluoro propanol, 1 and 1, and 5-trihydro perfluoro pentanol, 1, omega-trihydro perfluoro alcohol, etc. this, and 2, 2, 3, 3, and 3-pentafluoro propanol etc. can be mentioned, for example. The phosphazene compound of the general formula (1) which has desired a, b, x, and y value is obtained by changing suitably the class and the amount of phenols and the fluoro alcohols used in the case of manufacture.

[0008] In this invention, the phosphazene compound of a general formula (1) can be used as lubricant as it is, or the phosphazene compound of a general formula (1) may be dissolved and used for a suitable organic solvent. As an organic solvent, for example Aromatic hydrocarbon, such as toluene and a xylene, A methylene chloride, chloroform, 1,1,1-trichloroethane, Halogenated hydrocarbon, such as 1,1,2-trichloroethane and trichlorofluoroethane (chlorofluorocarbon 113), The ether, such as diethylether, dimethoxyethane, dioxane, and a tetrahydrofuran, Alicyclic hydrocarbon, such as ester, such as ethyl acetate, ethyl butylate, and amyl acetate, a cyclohexane, cycloheptane, and cyclooctane, dimethylformamide, dimethyl sulfoxide, two or more sorts of these mixed solvents, etc. can be mentioned.

[0009] It is used for the coat by the lubricant of this invention on a DLC protective coat, usually forming. Formation of the coat of this invention lubricant can be carried out with \*\* etc. according to a well-known approach. It faces applying the lubricant of this invention to the hard disk which has a DLC protective coat, and the approach of a spin coat, a DIP coat, etc. is adopted. Although especially the thickness is not restricted, it should just usually make about 10-200Å preferably about 10-50Å. In addition, since adjustment of thickness changes with the vapor pressure of an organic solvent, the concentration of the phosphazene compound of a general formula (1), drying temperature, etc., it can be carried out by choosing the organic solvent to be used suitably or adjusting concentration and drying temperature.

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## EXAMPLE

[Example] An example and the example of a comparison are given to below, and this invention is explained concretely.

After the hard disk was immersed, it took out, and dried for 30 minutes at 120 degrees C, and the coat of 20-30A of thickness was formed on the hard disk at the solution which dissolved compound (1)1g given in example 1 table 1 in toluene 500ml. The following trial was presented with this thing. The performance test of lubricant was carried out using the system drive converted so that coefficient of friction could be measured from the force concerning a head by measuring change of coefficient of friction at the time of starting by the CSS repeat test. The head started, where a disk front face is contacted, and the CSS cycle performed the stroke until a head stops again where a disk front face is contacted after the head has surfaced and reaching predetermined engine-speed 3600rpm in 33 seconds, and made this 1 cycle. The texture was made nothing, in order that a hard disk might be what produced the 200-300A DLC protective coat by plasma CVD and might raise surface smooth nature on the record medium produced by 3.5 inches sputtering. The head set the load to 7.5g by Monolithic MIG (metal in gap). The life judging of a CSS test was taken as the event of a dynamic friction coefficient ( $\mu$ ) exceeding 0.6.

[0011]

[A table 1]

		潤滑剤					低速摩	C S S 寿命	ディスクの状態
		化合物 (1)					擦係数	(サイクル)	
		a	b	x	y	R	初期	$\mu=0.6$	
実 施 例	1	1	1	1	3	H	0.183	20000	異常なし
	2	0.5	1.5	2	3	H	0.181	23000	異常なし
	3	1	1	2	3	H	0.184	25000	異常なし
	4	1	1	3	3	H	0.184	28000	異常なし
	5	1	1	4	3	H	0.198	26000	異常なし
	6	1	1	2	4	H	0.195	24000	異常なし
	7	1	1	2	3	CH <sub>3</sub>	0.190	24000	異常なし
	8	1	1	2	3	OCH <sub>3</sub>	0.197	22000	異常なし
	9	1	1	2	3	CF <sub>3</sub>	0.182	29000	異常なし
	10	1	1	3	3	CF <sub>3</sub>	0.185	32000	異常なし
	11	1	1	2	4	CH <sub>3</sub>	0.201	20000	異常なし
比 較 例	1	0	2	1	3	—	0.133	2600	起動 $\mu$ オーバー
	2	PFPE-OH					0.300	6000	起動 $\mu$ オーバー
	3	NF-10					0.120	2200	起動 $\mu$ オーバー
	4	なし					0.296	10	ヘッド付着、傷

[0012] The permutation location of R is the meta position.

PFPE-OH: F[CF(CF<sub>3</sub>)CF<sub>2</sub>O] nCF(CF<sub>3</sub>)CH<sub>2</sub>OHNF-10:[N=P(OCH<sub>2</sub>CF<sub>3</sub>)](OCH<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>) 3 of average molecular weight 2000 [about]

[Translation done.]

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G11B 5/72			G11B 5/72	
C10M137/16			C10M137/16	
// C10N 40:18				

審査請求 未請求 請求項の数 2 F D (全 4 頁)

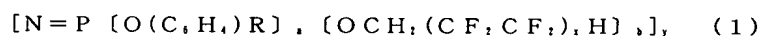
(21) 出願番号	特願平 10-41053	(71) 出願人	000146180 株式会社松村石油研究所 兵庫県西宮市芦原町 10 番 33 号
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(54) 【発明の名称】 ハード磁気ディスク用潤滑剤

(57) 【要約】

【課題】 良好な CSS 耐久性を有するハードディスク用潤滑剤を提供する。

【解決手段】 一般式 (1) で表されるホスファゼン化合物を有効成分とするハード磁気ディスク用潤滑剤。

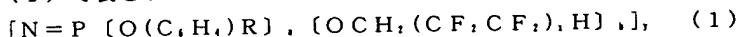


〔式中、R は水素原子、 $C_1 \sim 4$  のアルキル、 $C_1 \sim 4$  のアルコキシ、 $C_1 \sim 4$  のハロアルキルであり、a 及び b は 0

～ 2 の実数で  $a+b=2$  であり、x は 1、2、3 又は 4 であり、y は 3 又は 4 である。〕

## 【特許請求の範囲】

【請求項 1】 一般式 (1) で表されるホスファゼン化



〔式中、Rは水素原子、 $C_{1\sim 4}$ のアルキル、 $C_{1\sim 4}$ のアルコキシ、 $C_{1\sim 4}$ のハロアルキルであり、a及びbは0～2の実数で $a+b=2$ であり、xは1、2、3又は4であり、yは3又は4である。〕

【請求項 2】 炭素保護膜で表面被覆されたハード磁気ディスク用の潤滑剤である請求項 1 記載の潤滑剤。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、大容量記録媒体であるハード磁気ディスクの潤滑剤に関する。更に詳しくは、本発明は、使用開始時と停止時に記録媒体と記録・再生用素子が接触する構造となっているコンタクト・スタート・ストップ (CSS) 方式の記録装置において、記録媒体となるハード磁気ディスクの表面潤滑剤に関する。

【0002】

【従来の技術】インターネット、イントラネット、ローカルエリアネットワーク等が普及し、ネットワークにアクセスするだけで簡単に情報が取り出せるようになってきた。このようなマルチメディア時代を支えているものの一つに外部記憶装置がある。既存の大容量外部記憶装置としては、強度の高い円形基板 (ハードディスク) 上に記録媒体層を設け、このハードディスクを高速回転させて記録・再生用素子 (ヘッド) が作動する方式、いわゆる CSS 方式のものが一般的であり、ハードディスクとしては、固定式磁気ディスク、光ディスク、光磁気ディスク等がある。これらの中で最も普及しているものが固定式磁気ディスクを用いた装置である。

【0003】

【発明が解決しようとする課題】これら外部記憶装置のサイズを変えずに大容量化を行うには、例えば記録媒体層の面記録密度を増加する必要がある。このためには、ビットサイズを小さくし、ヘッドをできる限り記録媒体に近づけることが必要である。ヘッドとディスクとの間隔を小さくするためには、ディスク表面の凹凸を小さくせねばならず、例えば間隔を 100nm 以下にするには凹凸を 10nm 以下にせねばならない。そして、ディスク表面の平滑性を上げると、一方で、ヘッドがディスク面に吸着し易くなる。また、高速応答性を得るためには、ビット転送速度ひいてはディスクの回転速度を上げる必要がある。例えば 3.5 インチハードディスクの最高回転数は 5400～7200 rpm が必要で、ディスク周辺部のヘッド通過速度は 125 km/hr に達している。しかし、上記の様な変更は、何れもディスクとヘッドの接触確率と摩擦等を大幅に増加させ、信頼性を低下させることになる。

【0004】これらに対処し、ディスク表面とヘッドを

合物を主成分とするハード磁気ディスク用潤滑剤。

保護するには、ディスク保護膜表面への潤滑剤の塗布量を多くする方法が一番簡便である。しかしながら、潤滑剤の塗布量を多くすると潤滑膜の摺動抵抗が大きくなるのみならず、潤滑剤の吸着作用を増大し、スピンドルモーターの停止・焼損を引き起こす。摺動抵抗を低減するため、低粘度の潤滑剤を使用すると、ディスクの高速回転時に潤滑剤が保護膜上から移動・消失し、ディスクとヘッドの接触、破損を引き起こす。潤滑剤はごく簡単には、ハードディスク上に設けられている保護膜上に分子の厚みの均一な潤滑剤の膜を作って、ハードディスク回転時及び装置の起動・停止時に生じる摩擦及び摩擦を低減させている。ディスクとヘッドを保護するためには、摺動抵抗が小さく、保護膜との結合力が大きく、低摩擦係数で、化学的安定性、熱安定性、耐食性が大きく、-10℃以下での低温潤滑能力を有し、低蒸気圧で超薄膜化が可能な潤滑剤が必要である。ハードディスク用潤滑剤には、CSS 耐久性 2 万回以上で、摩擦係数の変化がないことである。即ち、CSS 繰り返しテストに於いて 2 万回を越えても、ヘッドの焼き付きやディスクに傷等の異常がなく、摩擦係数の変化が 0.3 以下であることが要求されている。

【0005】現行ハードディスクの表面保護膜には、化学的安定性、強度、超薄膜化、平滑性等の観点から、ダイヤモンド状炭素 (DLC、Diamond Like Carbon) 保護膜が用いられている。当該保護膜はその構造からも明らかな如く、大部分が炭素であることから、化学的結合性が小さく、付着力はわずかに混在する水素並びに窒素原子との水素結合やファンデルワールス力等の相互作用に因る他はない。そこで潤滑剤としては、パーフルオロアルキルポリエーテルオリゴマー (以下「PFPE」と略す) が一般的である (月刊トライボロジ、No. 99, 11 月号、37～38 頁、1995)。PFPE はフルオロカーボンに由来する低表面エネルギー、化学的不活性、低蒸気圧、熱安定性を備えているが、低表面エネルギー故に保護膜表面との結合力が弱く、ディスク回転の遠心力で潤滑剤が保護膜上から移動・消失してしまう欠点がある。これを抑えるため、第二成分の添加剤を使用しているが (USP 4871625)、PFPE のフルオロカーボンに由来する低相溶性のため、相分離を引き起こし、十分な効果が得られていないのが現状である。そこで、PFPE に結合性を付与するため、PFPE 主鎖の端部又は中央部に水酸基、アシルアミド基等の官能基を導入したもの (アウジモント社、FOMBL IN Z 誘導体) もあるが、これら活性水素を有する官能基はヘッドとの摩擦で化学的安定性を低下させる恐れがある。本発明の課題は良好な CSS 耐久性を有するハードディスク用潤滑剤を提供することにある。

## 【 0 0 0 6 】

【課題を解決するための手段】本発明は一般式 ( 1 ) で



〔式中、Rは水素原子、 $C_1\sim a$ のアルキル、 $C_1\sim a$ のアルコキシ、 $C_1\sim a$ のハロアルキルであり、a及びbは0～2の実数で $a+b=2$ であり、xは1、2、3又は4であり、yは3又は4である。〕

本発明化合物の良好なCSS耐久性は、既に特願昭57-47680号等の多数の先行文献に示されている化合物 ( 1 ) の良好なる潤滑性能と高極圧性能及びDLC保護膜への良好な付着力に基づくものである。ここでDLC保護膜への良好な付着力は、隣接するフッ素原子により分極されたフルオロカーボン末端の水素とDLC保護膜の水素並びに窒素原子との相互作用と、ホスファゼン環とDLC保護膜との相互作用の相乗効果によるものと考えられる。

## 【 0 0 0 7 】

【発明の実施の態様】本発明の一般式 ( 1 ) で表されるホスファゼン化合物において、Rの $C_1\sim a$ のアルキルとしてはメチル、エチル、プロピル、ブチル等を、 $C_1\sim a$ のアルコキシとしてはメトキシ、エトキシ、プロポキシ、ブトキシ等を、 $C_1\sim a$ のハロアルキルとしては上記アルキル基にフッ素、塩素、臭素が置換した基を挙げることができる。これらホスファゼン化合物は例えば、特開昭58-164698号公報、特開昭62-265394号公報、特開昭63-103428号公報、米国特許第4613548号明細書等に記載の公知化合物であり、例えばホスホニトリルハライドのオリゴマーとフェノール類のアルカリ金属塩、フルオロアルコール類のアルカリ金属塩とを反応させることにより製造できる。ここでホスホニトリルハライドのオリゴマーとしては、例えば、ホスホニトリルクロリドのトリマー、ホスホニトリルクロリドのテトラマー等やこれらの混合物等を挙げることができる。また、フェノール類としてはフェノール、メチルフェノール、メトキシフェノール、トリフルオロメトキシフェノール、3-ヒドロキシベンゾトリフルオリド、その他USP4613548号に記載のものを挙げることができる。フルオロアルコール類としては、例えば、1,1,3-トリヒドロパーフルオロプロパノール、1,1,5-トリヒドロパーフルオロペンタノール等の1,1, $\omega$ -トリヒドロパーフルオロアルコール等やこれと2,2,3,3,3-ペンタフルオロプロパノールとの混合物等を挙げることができる。製造の際、フェノール類及びフルオロアルコール類の種類と使用量を適宜変更することにより、所望のa、b、x、y値を有する一般式 ( 1 ) のホスファゼン化合物が得られる。

【 0 0 0 8 】本発明においては、一般式 ( 1 ) のホスファゼン化合物をそのまま潤滑剤として用いることができ、或いは一般式 ( 1 ) のホスファゼン化合物を適当な有機溶媒に溶解して用いてもよい。有機溶媒としては、

表されるホスファゼン化合物を有効成分とするハード磁気ディスク用潤滑剤に係る。

例えば、トルエン、キシレン等の芳香族炭化水素、メチレンクロライド、クロロホルム、1,1,1-トリクロロエタン、1,1,2-トリクロロエタン、トリクロロトリフルオロエタン ( フロン 1 1 3 ) 等のハロゲン化炭化水素、ジエチルエーテル、ジメトキシエタン、ジオキサン、テトラヒドロフラン等のエーテル、酢酸エチル、酪酸エチル、酢酸アミル等のエステル、シクロヘキサン、シクロヘプタン、シクロオクタン等の脂環式炭化水素、ジメチルホルムアミド、ジメチルスルホキシド、これらの2種以上の混合溶媒等を挙げることができる。

【 0 0 0 9 】本発明の潤滑剤は通常、その被膜をDLC保護膜の上に形成して使用される。本発明潤滑剤の被膜の形成は、公知の方法に従い、例えば、塗付等により実施できる。本発明の潤滑剤を、DLC保護膜を有するハードディスクに塗布するに際しては、スピンコート、ディップコート等の方法が採用される。その膜厚は特に制限されないが、通常10～200Å程度、好ましくは10～50Å程度とすればよい。尚、膜厚の調整は有機溶媒の蒸気圧、一般式 ( 1 ) のホスファゼン化合物の濃度、乾燥温度等によって変化するので、使用する有機溶媒を適宜選択したり、濃度や乾燥温度を調整することにより実施できる。

## 【 0 0 1 0 】

【実施例】以下に実施例及び比較例を挙げ、本発明を具体的に説明する。

## 実施例 1

表 1 に記載の化合物 ( 1 ) 1g をトルエン 500ml に溶解した溶液に、ハードディスクを浸漬した後、取り出して120℃で30分間乾燥し、ハードディスク上に、膜厚20～30Åの被膜を形成した。このものを下記の試験に供した。潤滑剤の性能試験は、ヘッドにかかる力から摩擦係数を測定できるように改造した実機ドライブを用い、CSS繰り返しテストによる起動時の摩擦係数の変化を測定することにより実施した。CSSサイクルはヘッドがディスク表面に接触した状態で始動し、ヘッドが浮上した状態で所定回転数3600rpmに達した後、再びヘッドがディスク表面に接触した状態で停止するまでの行程を33秒で行い、これを一サイクルとした。ハードディスクは3.5インチのスパッタリングで作製した記録媒体上にプラズマCVDで200～300ÅのDLC保護膜を作製したもので、表面平滑性を高めるため、テクスチャーはなしにした。ヘッドはモノリシックMIG ( metal in gap ) で荷重は7.5gとした。CSSテストの寿命判定は、動摩擦係数 ( $\mu$ ) が0.6を越えた時点とした。

## 【 0 0 1 1 】

## 【 表 1 】

		潤滑剤					低速摩	CSS寿命	ディスクの状態
		化合物 (1)					擦係数	(サイクル)	
		a	b	x	y	R	初期	$\mu=0.6$	
実 施 例	1	1	1	1	3	H	0.183	20000	異常なし
	2	0.5	1.5	2	3	H	0.181	23000	異常なし
	3	1	1	2	3	H	0.184	25000	異常なし
	4	1	1	3	3	H	0.184	28000	異常なし
	5	1	1	4	3	H	0.198	26000	異常なし
	6	1	1	2	4	H	0.195	24000	異常なし
	7	1	1	2	3	CH <sub>3</sub>	0.190	24000	異常なし
	8	1	1	2	3	OCH <sub>3</sub>	0.197	22000	異常なし
	9	1	1	2	3	CF <sub>3</sub>	0.182	29000	異常なし
	10	1	1	3	3	CF <sub>3</sub>	0.185	32000	異常なし
	11	1	1	2	4	CH <sub>3</sub>	0.201	20000	異常なし
比 較 例	1	0	2	1	3	—	0.133	2600	起動 $\mu$ オーバー
	2	PFPE-OH					0.300	6000	起動 $\mu$ オーバー
	3	NF-10					0.120	2200	起動 $\mu$ オーバー
	4	なし					0.296	10	ヘッド付着、傷

【0012】Rの置換位置はメタ位である。

PFPE-OH：平均分子量約2000のF〔CF(CF<sub>3</sub>)CF<sub>2</sub>O〕<sub>n</sub>CF(CF<sub>3</sub>)CH<sub>2</sub>OH

NF-10：〔N=P(OCH<sub>2</sub>CF<sub>3</sub>)(OCH<sub>2</sub>CF<sub>3</sub>C(F<sub>3</sub>))〕<sub>n</sub>

【0013】

【発明の効果】本発明によれば良好なCSS耐久性を有するハード磁気ディスク用潤滑剤を提供することができる。